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(54) Title: PREPARATIONS AND USES OF POLYFERRIC SULPHATE

(57) Abstract

A process for preparing a polymeric form of ferric sulphate wherein an acidic aqueous solution comprising ferrous sulphate is oxidised to form ferric sulphate in said solution in an oxidation stage at ambient pressure and in the absence of oxidation catalyst using at least one oxidising agent, said ferric sulphate subsequently being at least partially hydrolysed by addition to said solution of at least one base, the ferric sulphate being kept in contact with said base at the temperature selected for a time sufficient for polymerisation of the at least partially hydrolysed ferric sulphate. The polyferric sulphate (PFS) obtained by embodiments of such a process can be used as a coagulant or flocculant in water treatments for decolourising, purifying or reducing pollutants with improved performance compared to conventional ferric sulphate and aluminium sulphate treatments.

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PREPARATIONS AND USES OF POLYFERRIC SULPHATE

Chemical coagulants for drinking water, to purify and/or decolourise municipal water supplies for human consumption are known and include iron and aluminium-based inorganic coagulants.

Polyferric sulphate, PFS, is one known form of coagulant which has also been used to treat municipal and industrial waste waters to help remove, by flocculation, suspended organic waste matter. There is currently considerable interest in the more widespread application of PFS as coagulants. Because of its relative efficiency, PFS may need less chemical addition, it can have a greater removal capacity and may reduce the volumes of waste concentrates that require disposal or further treatments.

PFS is a known chemical and there are several patents describing methods for its preparation.

The present invention is concerned with methods for preparing polymeric forms of ferric sulphate, of which PFS is an example.

Essentially, the chemical can be prepared according to this invention by oxidising ferrous sulphate to ferric sulphate, and then carrying out a controlled, partial hydrolysis of the ferric sulphate to produce a heterogenous mixture of iron (III) hydrolysis species, $[Fe(OH)_x]^{(3-x)+}$, and polynuclear complexes of iron (III), $(Fe_m(OH)_x)_n^{(3m-x)n+}$. The functions of these species are to provide both colloid charge neutralization and polymer bridging between floc particles, leading in practice to a

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greater coagulating (and therefore, treatment) performance.

According to this invention there is provided a process for preparing a polymeric form of ferric sulphate wherein an acidic aqueous solution comprising ferrous sulphate is oxidised to form ferric sulphate in said solution in an oxidation stage at ambient pressure and in the absence of oxidation catalyst preferably using at least one oxidising agent from the following: ozone, nitric acid, peroxide, perchlorate and persulphate,

said ferric sulphate subsequently being at least partially hydrolysed by addition to said solution of at least one base, the ferric sulphate being kept in contact with said base at the temperature selected for a time sufficient for polymerisation of the at least partially hydrolysed ferric sulphate.

The ferrous sulphate solution may be rendered acidic by addition of e.g. sulphuric acid. This may usefully increase the level of sulphate ions in solution, without adding unwanted ionic species. The pH of the starting solution is preferably less than 2.0, more preferably in the range 0.8 to 1.5.

Preferably the oxidation stage is a one-step oxidation stage. Preferred oxidising agents include peroxide and nitric acid. It is possible to use strong concentrated or even fuming nitric acid.

Accordingly the concentration of the nitric acid used in the oxidation stage is preferably at least 50% by volume, more preferably at least 70% by volume although nitric acid as concentrated as 90% by volume can be used.

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It is also preferred to use peroxide as an oxidising agent and more preferably hydrogen peroxide. The strength of the hydrogen peroxide used, as with the option of nitric acid mentioned above, may be dictated by the economics of the cost of raw materials, oxidation temperature and oxidation time.

Thus a stronger oxidising agent will most likely allow a shorter oxidation time and/or a lower oxidation reaction temperature. With hydrogen peroxide at very strong concentration, perhaps of the order 30 volumes, it may even be possible to effect the oxidation stage at ambient temperatures, for example at a temperature in the range of 15° to 25°C. Oxidation temperatures when using hydrogen peroxide may be 70°C or lower, such as 60°C or lower, preferably no higher than 50°C.

Oxidation temperatures when using nitric acid as the oxidising agent, may be 110°C or lower, such as 90°C or lower, preferably no higher than 70°C (which temperature may be possible when using the very concentrated, fuming nitric acid having a strength of at least 90%).

The oxidation time for a preferred one-step oxidation stage may be up to 3 hours, for example up to 2 hours, more preferably 1.75 to 1 hours. The oxidation time, as with the oxidation temperature, may depend upon the nature and strength of the oxidising agent used and the molar ratio of oxidant : iron $[Fe^{2+}]$.

It is preferred to carry out the oxidation such that there is a near-complete oxidation of ferrous $[Fe^{2+}]$ ions to ferric $[Fe^{3+}]$ ions. In consequence it is preferable

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for the concentration of ferrous ions in the solution after the oxidation step to be less than 2.5% (Fe^{2+}/Fe^{3+}), more preferably less than 1.25% (Fe^{2+}/Fe^{3+}), most preferably less than 0.25% (Fe^{2+}/Fe^{3+}).

The molar ratio of oxidant : ferrous ions in the solution, for the oxidation stage may depend upon economics and the desire to bring about the aforementioned near-complete oxidation of ferrous ions in aqueous solution, to ferric ions in the same solution. The molar ratio may also be influenced by the choice of oxidising agent and its relative strength, the oxidation temperature required or otherwise selected and the oxidation time necessary for this near-complete oxidation.

For example, when using nitric acid as the oxidising agent at say 90°C, at a concentration of 70%, the preferred molar ratio of oxidant : ferrous ions present in the aqueous solution is no higher than 2:1, more preferably no higher than 1.5:1, most preferably about 1.13:1.

When using hydrogen peroxide as the oxidising agent at say 50°C at a strength of 30 vols, then the preferred molar ratio of oxidant : ferrous ions present in the aqueous solution is no higher than 3:1 preferably no higher than 2:1 most preferably about 1.81:1. These most preferred ratios have been found to achieve a near-complete oxidation of ferrous ions to ferric ions, i.e. $<0.5g[Fe^{2+}]$ per litre after oxidation, when the oxidation has been allowed to proceed for about 1½ hours.

We have also used this concentrated form of hydrogen peroxide (30 vols) in the oxidation stage, with a

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larger molar excess of oxidant : ferrous ions, at lower temperatures, even at ambient temperatures of about 20°C. For example a molar ratio of 2.9:1 oxidant : ferrous ions led to near-complete oxidation even in the absence of oxidation catalyst and at ambient (atmospheric) levels of pressure. Thus additional heat energy input for the oxidation may be avoided.

In the secondary stage of at least partial hydrolysis, it is possible simply to add one or more bases to the ferric sulphate which has been formed in aqueous solution. The base can be strong or weak inorganic bases such as a hydroxide or bicarbonate of an alkali metal. In particular sodium hydroxide or sodium bicarbonate can be used. The hydrolysis stage can be likened to an 'aging' step during which iron (III) hydrolysis species, $[Fe(OH)_x]^{(3-x)+}$ and polynuclear complexes of iron (III), $[Fe_m(OH)_x]_n^{(3m-x)n+}$ form as a polymeric form of ferric sulphate, often referred to in the technical field as polyferric sulphate (PFS).

The hydrolysis stage is most preferably carried out immediately after a one-step oxidation process, by simple addition of base to the ferric ions which have been formed in the acidic, aqueous solution. It has not been found necessary to remove or even otherwise purify the ferric sulphate formed after the oxidation stage.

The amount of base added is preferably such as to provide an $[OH]^-$: $[Fe]^{3+}$ molar ratio in the finished product obtained by the process, the polymeric form of ferric sulphate, of at least 0.1, preferably at least 0.2,

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more preferably 0.25 - 0.45:1.0. We have found that an actual ratio of 0.3:1 of $[\text{OH}]^-$: $[\text{Fe}]^{3+}$ in the final product gives a desirable optimum in terms of performance, costs and stability.

The amount of iron in the final polymeric form of ferric sulphate produced by the method can be for example, up to $30\text{g}.\text{l}^{-1}$ of iron, preferably up to $40\text{g}.\text{l}^{-1}$ of iron, even more preferably up to $200\text{g}.\text{l}^{-1}$ of iron and most preferably upto $350\text{g}.\text{l}^{-1}$ of iron.

Elevated temperature may be necessary for the hydrolysis/polymerisation to proceed to a satisfactory $[\text{OH}]^-$: $[\text{Fe}]^{3+}$ ratio, for example a temperature of at least 30°C , preferably at least 40°C more preferably 45°C or higher, such as 50°C . Moreover the ferric sulphate can be kept in contact with the base for a time sufficient to obtain the aforementioned ratios of hydroxyl : ferric ions in the final polymeric product. Up to 3 hours may be needed at 50°C , preferably at least 2 hours.

The polyferric sulphate (PFS) obtained is usually in the form of a liquid solution which may not require separation or purification prior to use.

In use the polymeric form of ferric sulphate obtained, hereinafter also referred to for convenience as 'polyferric sulphate' and abbreviated as PFS can be used as a coagulant or flocculant to help purify and/or decolourise water for drinking water supplies and/or to reduce pollutants be they organic or inorganic, nitrogen- or phosphorus-containing such pollutants in municipal and/or industrial wastewaters.

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The PFS obtained by processes according to the invention can be more economical in manufacture and/or confer better performance than PFS obtained by other commercially established procedures.

EXAMPLES 1 and 2 - PREPARATION

Example 1

The example described as follows is for the preparation of 500mL solutions of PFS with a Fe(III) concentration of 40 g/L, using nitric acid as an oxidant.

Prescription:

1. FeSO ₄ .7H ₂ O (100%)	100g
2. H ₂ SO ₄ (98%)	8.2 mL
3. HNO ₃ (70%)	18.0 mL
4. Water	214.5 mL
5. NaHCO ₃ (0.5N)	214.0 mL

Preparation procedure:

The ferrous sulphate, sulphuric acid and the water in the prescribed amounts were added to a one litre reactor with a speed controlled mixer. The reaction temperature was controlled by an electromantle. Then, the temperature of the mixed solutions was raised to 60 (± 0.2) °C accompanied by vigorous stirring. Nitric acid was added to the mixed solutions gently. After the addition of the nitric acid, the reaction temperature was raised to and kept at 90 (± 0.2) °C with continuing vigorous stirring, until more than 99% of ferrous iron has been oxidized to ferric iron (after approximately 1.5 to 2.0 hours). The residual concentrations of ferrous iron were detected by the 1, 10 - phenanthrene calorimetric method. The reaction temperature

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was then reduced to and kept at 50 (± 0.2) °C. The sodium bicarbonate solution was added into the reaction solutions, and the addition rate was controlled to allow that all NaHCO_3 solution was added within a 30 minute period. Finally, the reaction solutions were maintained at a temperature of 50 (± 0.2) °C for another 1.5 hour period of aging. The PFS solution is thus prepared and, after cooling to room temperature is ready for use.

Properties of the prepared PFS:

$[\text{Fe(III)}] = 40 \text{ g/L}$, $[\text{Fe(II)}] \leq 0.2 \text{ g/L}$, OH/Fe (molar ratio) = 0.3, $\text{pH} = 0.9 - 1.1$,

Average electrophoresis mobility = $6 \pm 0.2 \mu\text{m cm/V s}$,

Size distribution of the molecular species in the PFS solution are:

low MW species ($< 0.5\text{K}$) = 20.0% (by weight of Fe),

medium MW species ($0.5 - 10\text{K}$) = 70.0% (by weight of Fe),

large MW species ($> 10\text{K}$) = 10.0% (by weight of Fe).

Stability:

The PFS solutions prepared by this method are stable over at least a 6 month stored period.

Example 2

The example described as follows is for the preparation of 500 mL solutions of PFS with a Fe(III) concentration of 40 g/L, using hydrogen peroxide as an oxidant.

Prescription:

1. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (100%) 100 g
2. H_2SO_4 (98%) 8.2 mL
3. H_2O_2 (30%) 20.0 mL
4. Water 212.5 mL
5. NaHCO_3 (0.5N) 214.0 mL

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Preparation procedure:

The ferrous sulphate, sulphuric acid and the water in the prescribed amounts were added to the one litre reactor, and the reaction temperature was controlled by an electromantle. Both the reactor and the electromantle were the same as used in the Example 1. The temperature of the mixed solutions was then raised to 40 (± 0.2) °C accompanied by vigorous stirring. H_2O_2 was added to the reaction solutions gently. After the addition of the hydrogen peroxide, the reaction temperature was raised to and kept at 50 (± 0.2) °C, and the oxidation process continued, until more than 99% of ferrous iron has been oxidized to ferric iron (after approximately 1.5 to 2.0 hours). The residual concentrations of ferrous iron were detected by the same method as described in the Example 1. The reaction temperature was kept at 50 (± 0.2) °C to carry out the aging process. The sodium bicarbonate solution was added into the reaction solutions, and the addition rate was controlled to allow that all $NaHCO_3$ solution was added within a 30 minute period. Finally, the reaction solutions were maintained at a temperature of 50 (± 0.2) °C for another 1.5 hour period of aging. The PFS solution is thus prepared and, after cooling to room temperature, is ready for use.

Properties of the prepared PFS:

$[Fe(III)] = 40 \text{ g/L}$, $[Fe(II)] \leq 0.2 \text{ g/L}$, OH/Fe (molar ratio) = 0.3, $pH = 1.0 - 1.1$.

Average electrophoresis mobility = $6 \pm 0.2 \mu\text{m cm} / \text{V s}$,

Size distribution of the molecular species in the PFS solutions are:

low MW species ($< 0.5\text{K}$) = 19.5% (by weight of Fe),

medium MW species ($0.5 - 10\text{K}$) = 69.0% (by weight of Fe),

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higher MW species (> 10K) = 11.5% (by weight of Fe).

Stability:

The PFS solutions prepared by this method are stable over at least a 6 month stored period.

EXAMPLES 3 to 8

PFS solutions prepared by the methods described in the Examples 1 and 2 have been used as a coagulant for the treatment of algal-laden and upland coloured surface waters in laboratory test and pilot-plant scale experiments. For the laboratory jar test experiments, a six-beaker jar test apparatus was used with each beaker containing either 300 mL of real or model algal waters, or 500 mL of simulated coloured waters. The fast mixing time was 3 min at a paddle speed of 300 rpm, the flocculation period was 25 min at a paddle speed of 35 rpm, and the sedimentation period was 1 hour. Supernatant samples after settling were withdrawn for analysis of algal cells, turbidity, UV absorbance, DOC, colour, residuals of Fe, Mn and Al. The coagulation pH required was achieved by prior addition of either HCl or NaOH, and the solution pH was checked during the mixing and flocculation periods. To evaluate the coagulation performance at lower water temperatures (4°C), a special constant temperature bath was used with the jar test beakers. The low temperature of 4°C (± 0.2) was maintained throughout the whole coagulation process and the one hour settling period.

Pilot-plant experiments were undertaken which comprised the processes of pre-ozonation, coagulation, flocculation, dissolved-air flotation (DAF), sand

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filtration, intermediate ozonation and either GAC or BAC. In the test period of about four weeks, the pilot plant was operated under the conditions of with and without application of ozone, with coagulants of either PFS or ferric sulphate (FS) for three doses (1,3,5 mg/L as Fe), and at a constant pH of 7.5 Raw water flow rate was 2 m³/hr. The pre-ozone dose and the contact time were 1.0 mg/L and 7.0 min, respectively; and the intermediate ozone dose was set to achieve a residual O₃ concentration of 0.25 mg/L after a contact time of 8.0 min. A separate set of samples was analysed to identify the kinds of algal species and to measure the total algal concentrations before and after treatment.

Table 1 presents example 3 using PFS and other comparative results (FS = ferric sulphate, AS = aluminium sulphate) for the treatment of two algal model waters in laboratory tests with the coagulants PFS, FS and AS at 18°C and at pH 7.5, for a given dose of 0.2 mM as Fe or Al. It can be seen that the coagulation performance of PFS in removing algae, turbidity, DOC, etc. was clearly superior to the other two conventional coagulants.

Table 2 summarises results with PFS (Example 4), FS and AS (both comparative) for the treatment of coloured waters at 18 and 4°C. It can be seen from Table 2. that under the optimum coagulation conditions at 18°C, the removal efficiency achieved by the three coagulants was close. However, the required PFS dose was the lowest (0.107 mM as Fe), compared to FS (0.143 mM as Fe), and AS (0.185 mM as Al), to achieve similar removal percentages. In

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addition, as shown in Table 2, the coagulation performance of PFS did not appear to be influenced significantly by low water temperatures. For AS and FS, however, low water temperature appeared to have an adverse effect on the removals of UV-Abs and DOC; but the removals of colour were slightly reduced. Residual concentrations of FS and AS were slightly increased at low water temperatures.

Tables 3A and 3B show results from the pilot-plant experiments concerning the raw water qualities and removal efficiencies by DAF (Table 3 A) and by DAF and sand filters (Table 3B). PFS (Examples 5 to 8) displayed a much greater treatment performance in removing algae, turbidity, colour, TOC and UV-absorbance (254 nm). The removal percentages achieved by PFS at a dose of 3 mg/L were either similar or even superior to those achieved by FS at 5 mg/L, indicating that coagulant dosing costs may be reduced for the same treated water quality.

Table 1. Comparison of the treatment performance of PFS, FS and AS at 18°C (Algal model waters)

Coagulants	Total cell removal%		DOC removal%	Turbidity removal%	UV-Abs (254nm) removal%	Vis-Abs (420nm) removal%	Colloid (floc) charge ^a	X	Y
	X*	Y†							
Example 3	PFS	96	86	61	45	88	79	50	48
	FS	80	61	33	24	69	60	40	26.5
	AS	90	70	52	32	84	72	45	40

* The unit is (meq L⁻¹ 10⁻⁴).
Coagulant dose for X and Y is 0.20 and AS as Al³⁺ or Fe³⁺.

• X - The water quality characteristics of *Asterionella* model waters:
Total cell conc. = 4.8·10⁴ cells mL⁻¹.
DOC = 2.5 ppm, UV-Abs (254 nm)=9.6 m⁻¹.
pH=8.3, Turbidity = 4 NTU,
Colloid charge = -92 meq L⁻¹ 10⁻⁴.

† Y - The water quality characteristics of synthetic algal waters (*Asterionella* 'model' water + 2mg/L humic substances):
Total cell conc. = 5.0·10⁴ cells mL⁻¹.
DOC = 4.8 ppm, UV-Abs (254 nm)=21.0 m⁻¹.
pH = 7.92, Turbidity = 4.5 NTU,
Colloid charge = -115 meq L⁻¹ 10⁻⁴.

Table 2. Comparison of the treatment performance of PFS, FS and AS at 18°C and 4°C (Coloured waters)

Coagulant	Dose* (mg/L AS or Al)	pH†	Colour (420nm) R%	UV-Abs (254 nm) R%		DOC R%	Residual Fe (mg/L)	Residual Al (mg/L)
				18°C	4°C			
Example 4	PFS	0.107	4	92.0	91.3	83.2	80.3	78.8 0.09
	FS	0.143	4	91.1	89.5	84.8	80.5	80.2 0.165 0.180
	AS	0.185	5	92.0	91.4	82.5	75.7	75.4 0.064 0.074
	Raw water	—	8.1	5.62 m ⁻¹	38.8 m ⁻¹	8.2 mg/L	0.05 mg/L	0.14 mg/L

* The coagulation pH and coagulant doses were selected in terms of the optimal pH and minimum dose required to achieve >90% colour removal, >80% UV removal and >75% DOC removal at 18°C.

Table 3A Comparison of coagulation efficiency of PFS and FS in the pilot-plant experiments (by DAF.)

Running conditions	UV (254 nm) (m ⁻¹)		TOC (mg/L)		Colour (400 nm) (m ⁻¹)		Turbidity (NTU)	
	Raw water	R. %	Raw water	R. %	Raw water	R. %	Raw water	R. %
Example 5	FS, 3 mg/L, no O ₃	11.0	13.64	6.17	10.8	12.0	36.67	2.5
	PFS, 3 mg/L, no O ₃	11.5	26.10	6.38	21.0	13.3	51.43	2.6
Example 6	FS, 5 mg/L, no O ₃	12.0	20.83	6.18	17.40	11.4	40.0	2.6
	PFS, 5 mg/L, no O ₃	12.5	28.0	5.54	22.6	12.54	48.68	2.5

* R. % = Percentage removed.

Table 3B Comparison of coagulation efficiency of PFS and FS in the pilot-plant experiments. (by DAF and sand filters.)

Running conditions	UV (254 nm) (m ⁻¹)		TOC (mg/L)		Colour (400 nm) (m ⁻¹)		Turbidity (NTU)		A _{cat} (cells/ml)	
	Raw water	R. %	Raw water	R. %	Raw water	R. %	Raw water	R. %	Raw water	R. %
Example 7	FS, 1 mg/L, no O ₃	11.0	18.18	6.17	21.90	12.0	39.83	2.5	64.8	79300
	PFS, 3 mg/L, no O ₃	11.5	30.43	6.38	24.76	13.3	53.23	2.6	73.0	249200
Example 8	FS, 5 mg/L, no O ₃	12.0	25.0	6.18	21.20	11.4	50.0	2.6	61.5	80320
	PFS, 5 mg/L, no O ₃	12.5	36.0	5.54	26.68	12.54	55.82	2.5	69.2	206322

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CLAIMS

1. A process for preparing a polymeric form of ferric sulphate wherein an acidic aqueous solution comprising ferrous sulphate is oxidised to form ferric sulphate in said solution in an oxidation stage at ambient pressure and in the absence of oxidation catalyst using at least one oxidising agent, said ferric sulphate subsequently being at least partially hydrolysed by addition to said solution of at least one base, the ferric sulphate being kept in contact with said base at the temperature selected for a time sufficient for polymerisation of the at least partially hydrolysed ferric sulphate.
2. A process as claimed in claim 1 wherein the oxidising agent comprises one or more of the following: ozone, nitric acid, peroxide, perchlorate and persulphate.
3. A process as claimed in claim 1 or 2, wherein the aqueous solution comprising ferrous sulphate further comprises sulphuric acid.
4. A process as claimed in any preceding claim wherein the pH of the aqueous solution prior to oxidation is less than 2.0.
5. A process as claimed in claim 4 wherein the pH is 0.8

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to 1.5.

6. A process as claimed in any preceding claim wherein the oxidation stage is a one-step oxidation stage.

7. A process as claimed in any preceding claim wherein the oxidising agent comprises nitric acid and/or peroxide such as hydrogen peroxide.

8. A process as claimed in any preceding claim wherein the oxidation temperature is 110°C or lower, such as 90°C or lower, or 70°C or lower.

9. A process as claimed in any preceding claim wherein the oxidation step is effected at a temperature between 15°C to 50°C.

10. A process as claimed in any preceding claim wherein the oxidation time for the oxidation step is up to 3 hours, preferably up to 2 hours, more preferably up to 1.75 hrs, most preferably up to 1 hr.

11. A process as claimed in any preceding claim wherein after the oxidation step the concentration of ferrous ions in solution is less than 2.5% $\text{Fe}^{2+}/\text{Fe}^{3+}$; preferably less than 1.25% $\text{Fe}^{2+}/\text{Fe}^{3+}$, more preferably less than 0.25% $\text{Fe}^{2+}/\text{Fe}^{3+}$.

12. A process as claimed in any preceding claim wherein the

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base comprises a hydroxide or bicarbonate of an alkali metal.

13. A process as claimed in any preceding claim wherein, during the hydrolysis step, iron (III) hydrolysis species $[\text{Fe}(\text{OH})_x]^{(3-x)+}$ and polynuclear complexes of iron (III) $[\text{Fe}_{(m)}(\text{OH})_x]_n^{(3m-x)n+}$ form as the polymeric form of ferric sulphate.

14. A process as claimed in any preceding claim wherein the hydrolysis stage is carried out immediately after the oxidation stage without removing or otherwise purifying the ferric sulphate formed after the oxidation stage.

15. A process as claimed in any preceding claim wherein in the finished product obtained by the process, the molar ratio of $[\text{OH}]^-$ to $[\text{Fe}^{3+}]$ is at least 0.1 : 1, preferably 0.2 : 1, more preferably 0.25 : 1, more preferably 0.1 - 0.45 : 1.

16. A process as claimed in any preceding claim wherein the hydrolysis stage is carried out at a temperature up to 50°C for a time up to 3 hours.

17. Use of polyferric sulphate (PFS) obtained by a process as claimed in any preceding claim as a coagulant or flocculant.

18. A method of treating water which comprises adding to the water a product obtained by a process as claimed in any

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one of claims 1 to 16.

19. A method as claimed in claim 18 which is a method of purifying and/or decolourising water.

20. A method as claimed in claim 18 which is a method of reducing pollutants in industrial and/or municipal wastewaters.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/GB 95/00483

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01G49/14 C02F1/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01G C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AU,A,464 517 (NITTETSU MINING CO) 28 August 1975 see the whole document ----	1-3,12, 17
A	FR,A,1 518 716 (SOC. DES ACCUMULATEURS FIXES ET DE TRACTION) 29 March 1968 see the whole document ----	1-3
A	US,A,2 905 533 (C.S. WEBB) 22 September 1959 see the whole document -----	1,8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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1 Date of the actual completion of the international search	Date of mailing of the international search report
6 July 1995	26.07.95
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer LIBBERECHT, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No

PCT/GB 95/00483

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
AU-A-464517	28-08-75	AU-A- 7174174	28-08-75
FR-A-1518716		NONE	
US-A-2905533	22-09-59	NONE	